CHARACTERISTICS OF COAL LIQUIDS
HYDROPROCESSED IN CONTINUOUS HYDROTREATER

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INTRODUCTION

The commercial production of hydrocarbon liquids from coal will significantly lessen the nation's long-term dependence on foreign crude oil. Coal liquefaction products are rich in aromatics but low in paraffins and usually contain substantial quantities of nondistillable, high-molecular-weight material and unacceptable levels of sulfur and nitrogen. Upgrading of coal liquids, therefore, is required to hydroprocess the heavy ends into lower-molecular-weight distillate that has the minimum possible content of sulfur and nitrogen. Catalytic hydroprocessing of heavy fossil fuels is normally effected by hydrotreating in the presence of catalysts like cobalt molybdate or nickel molybdate at 5-25 MPa and 575-725 K.[1] The common problems that can be encountered are rapid deactivation of catalyst, difficulty of hydrogenating aromatics, insufficient removal of nitrogen, and high consumption of hydrogen. Recent data on upgrading of blends of SRC-I and coal-derived creosote oil showed that modified Shell 324 Ni-Mo catalyst gave good performance in removing nitrogen.[2] In the present work, coal liquids hydroprocessed in a continuous hydrotreater over Ni-Mo catalysts under varying process severities were characterized to study variations in chemical constituents and physical properties of the coal liquid.

EXPERIMENTAL

A 30-70 blend of SRC-I with SRC-II distillate (453-665 K) produced from Western Kentucky bituminous coal was used as the feedstock. Hydrotreating experiments were carried out in a trickle-bed reactor of 17.4-mm i.d. and 1.2-m long with 530-mm bed length. The catalyst bed was placed in the midsection of reactor tube. Above and below the bed, Pyrex glass beads of 3-mm diameter were placed to serve as preheating and calming zones, respectively. Prior to the hydrotreating, the catalyst was pre-sulfided in situ with a H_2/H_2S stream containing 10 vol % H_2S at 616 K for 4 hours. The reactor temperature was maintained by a seven-zone furnace controlled by seven separate controllers to achieve $\pm$ 1 centigrade degree control. The catalysts used were Shell 324 Ni-Mo (0.84-mm extrudate), Nalco NM-504 (0.84-mm extrudate), and Ni-Mo catalysts prepared on Davison Y-alumina (0.59-1.0 mm granules). The ratio of catalyst bed length to particle size is sufficiently large (>550) that channelling and backmixing effects in the reactor appear to be minimized and the reproducibility of the data is good.[3] The process conditions were the following: H_2 pressure -- 13.8 MPa; temperature -- 672 K; liquid hourly space velocity (LHSV) -- 0.25-1.25 cm^3 feed/hr-cm^3 catalyst; and hydrogen feed rate -- 1335 m^3 H_2/m^3 oil (~7500 scf/bbl).

Product analysis included specific gravity, viscosity, asphaltenes, benzene insolubles, and elemental analysis. The gas stream was metered and sampled for mass spectrometric analysis. Hydrogen consumption values were calculated from elemental analysis. Mass spectra of coal liquids were obtained on a Consolidated Electrodynamics (CEC)-103B low voltage mass spectrometer and a CEC-21-110B high resolution mass spectrometer (1/10,000 resolution). Proton magnetic resonance spectra were obtained with a 100-MHz Varian XL-100 NMR spectrometer with tetramethylsilane as internal reference. Light and middle fractions of the hydrotreated products were separated by a Pope wiped film molecular still and analyzed for hydrocarbon types by fluorescence indicator adsorption (ASTM D 1319-77) in a silica gel column. The GC-MS analysis of aromatics and saturates was performed using a Hewlett-Packard 5985 mass spectrometer and a 11-m x 0.30-mm glass capillary column wall-coated with SE-52.

The column was temperature-programmed from 308 to 523 K at 2 degrees centigrade per minute.

RESULTS AND DISCUSSION

The elemental analysis and physical properties of the feed, a thermal-treated product obtained over alumina bed, and a hydrotreated product obtained over Shell 324 Ni-Mo catalyst bed are shown in Table 1. The products were obtained at the experimental conditions of 13.8 MPa, 672 K, and 0.5 LHSV. The thermal treatment of the blend of SRC-I with SRC-II over alumina in the absence of metal catalysts reduced the benzene insoluble content and the viscosity moderately, but did not affect the nitrogen content or other characteristics of the coal liquid significantly. The hydrogen consumption was very low. In comparison, the hydrotreating of the coal liquid in the presence of Shell Ni-Mo catalyst resulted in significant reduction of asphaltene, benzene insolubles, viscosity, and heteroatom contents (N, S, and O) at a hydrogen consumption of 3.77 wt % based on coal liquid feed. Nearly 80% of pentane insolubles (asphaltene + benzene insolubles) was converted to lower-molecular-weight material. The hydrotreating with the other Ni-Mo catalysts also yielded products having similar properties.

The efficiency of hydrotreating coal liquids depends on the activity of the catalyst towards the high-molecular-weight, pentane-insoluble material, which contains the highest concentrations of heteroatoms. Figure 1 shows the nitrogen removal as a function of process severity, expressed by hydrogen consumption, and the relationship of nitrogen content and hydrogen content in the liquid products. Data points were obtained from hydrotreating experiments using the different Ni-Mo catalysts. The linearity of the plot of nitrogen removal versus hydrogen consumption suggests that all the catalysts have similar activity. The plot can be used to evaluate the nitrogen removal activity of a catalyst and to determine the efficiency of hydrogen utilization. A highly active catalyst would give data points significantly above the linear curve, indicating the effective nitrogen removal at low process severity.

The linear relationship between the nitrogen and hydrogen contents of the liquid products shown in the bottom plot suggests that nitrogen removal accompanies hydrogen addition to aromatics in the coal liquid. Nitrogen removal from polycyclic aromatics does not take place until ring saturation has occurred.[4] Recent studies on model compounds suggest that the naphthalene moiety, having a lower resonance energy per ring than benzene, undergoes hydrogenation more rapidly than the benzene moiety.[5] The hydrogenation of aromatic compounds is considered to be among the slowest of hydroprocessing reactions occurring in the coal liquids upgrading process.

It is also of interest to examine the relationship between nitrogen content and specific gravity of the liquid products. The data points in Figure 5 include those obtained at varying process severities with temperatures ranging from 672 to 694 K and LHSV varying from 0.25 to 1.25 hr^{-1}. The feedstock has a nitrogen content of 1.31 wt %, and the liquid products have values covering a broad range. The nitrogen content decreases linearly with the specific gravity of the liquid products until a point near 0.25 wt % nitrogen and 0.94 specific gravity, but further decrease of nitrogen content becomes difficult even though specific gravity is further reduced significantly. The implication is that upon hydrocracking, certain types of nitrogen-containing polycyclic compounds are formed and that further nitrogen removal is more difficult to achieve even under severe processing conditions with very high hydrogen consumption. The key is to develop a catalyst that is effective in hydrogenating these types of nitrogen-containing polycyclic compounds at low temperature. The ideal catalyst would probably have activity for removing nitrogen without saturating aromatic rings.

Mass spectra of the feedstock and products from thermal treatment and hydro-treatment over Shell catalyst were obtained on a low voltage mass spectrometer and a high resolution mass spectrometer (1/10,000 resolution). Table 2 shows the analysis

for polynuclear aromatic (PNA) compounds based on total ionization at 573 K and 10^{-6} torr; naphthalenes in the feedstock were drastically reduced by hydrotreating and were presumably converted to tetralins and/or indans. The results from the high resolution mass spectrometer were presented by the graphical method of Mentser and Sharkey,[6] shown in Figure 2, for hydrocarbon components (C_xH_y). The utility of these plots is to determine the classes of hydrocarbon that are present in the sample. The limiting H/C values for the molecular ions of PNA's in the hydrotreated product are greater than the respective values for those in the feedstock, indicating increased hydrogenation by hydrotreating. These data combined with the low voltage mass spectrometric data suggest the sharp decrease in the concentration of aromatics and some corresponding increase in the concentrations of hydroaromatics and alkylated aromatics. Similar plots of hydrogen- carbon distribution in heteroatom components having formulas C_xH_yN and C_xH_yO are shown in Figures 3 and 4, respectively. Large parts of the nitrogen-containing compounds having C_5-C_{15} range in the feedstock are removed after hydrotreating. Only small concentrations of nitrogen-containing C_5-C_9 cyclic compounds having decreased H/C values were found in the hydrotreated product. Most of the molecular species of phenols in the feedstock were removed by hydro-treating, and some of two- and three-ring phenols were also reduced by the thermal treatment (Figure 4).

Distributions of oxygen and hydrogen in the thermal-treated and hydrotreated products, as determined by IR and PMR analyses, respectively, are summarized in Table 3. Most of the phenolic OH and carbazolic NH in the feedstock are removed by hydrotreating, but the remaining oxygen in ether forms is difficult to remove. On hydrotreating, the aromatic hydrogen content decreases, hydrogen is added to aromatic rings to form hydroaromatic structures, and the bulk of aliphatic hydrogen is added at positions further from the aromatic ring than the α position. The variation of the PMR spectra is shown in Figure 6. These results are in accord with the above mass spectrometric data and are also in agreement with the earlier study reported by Tewari et al.[7]

The hydrotreating condition at 13.8 MPa, 672 K, and 0.5 LHSV is not too severe, but the light and middle distillates of the upgraded product are of fairly high quality in that the nitrogen and sulfur contents are fairly low. For example, the typical sulfur and nitrogen distribution in the hydrotreated product with Shell Ni-Mo catalyst is shown in Table 4. The upgraded product with Shell Ni-Mo catalyst was separated into three fractions by a Pope wiped film molecular still. The light and middle fractions were analyzed for hydrocarbon type by fluorescence indicator adsorption. Aromatics and saturates are the major components. The GC-MS chromatograms of the aromatics and saturates for the naphtha fraction (IBP-477K), Figure 7, show that the major components tentatively identified are one- and two-ring compounds. The aromatics were mostly toluene, alkyl (up to C_3) benzenes, xylenes, tetralin, and alkyl (up to C_2) tetralins. The saturates are mostly cyclohexane and alkyl (up to C_4) cyclohexanes. The naphtha fraction of the upgraded product was also found to be fairly stable. After an aging test under oxygen atmosphere at 363 K for one week, no precipitation or color change was observed. In comparison, the naphtha fraction of untreated SRC-II gave a 12 wt % precipitate and was a brownish color after the same aging test.

In conclusion, the removal of nitrogen accompanies hydrogen addition to aromatics in the coal liquid, and the hydrogenation of nitrogen-containing polycyclic compounds having lower H/C values is among the slowest of hydroprocessing reactions to accomplish. The linear plot of nitrogen removal versus hydrogen consumption for reference catalysts provides a useful reference source for evaluating the nitrogen removal activity and the hydrogen utilization efficiency of a new catalyst. Along with the decrease in heteroatoms, asphaltenes, and aromatics, and the corresponding increase in hydro-aromatics and alkyl aromatics, the phenolic OH and carbazolic NH contents were drastically reduced by hydrotreating.

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TABLE 1.   COMPARISON OF THERMAL-TREATED AND HYDROTREATED PRODUCTS
(13.8 MPa, 672 K, 0.5 LHSV)

	Feedstock SRC I/II	Thermal-Treated HR 8-1	Hydrotreated HR 6-1
Catalyst	--	Alumina	Shell Ni-Mo
Sp. Gravity, 289/289 K	1.07	1.06	0.94
Viscosity, CPS at 311 K	181	55	6.5
Asphaltene, wt %	16.0	16.5	5.0
Benzene Insol., wt %	10.8	7.4	0.3
Molecular Weight[a]	236	220	207
Elemental Analysis, wt %			
C	85.52	86.02	85.68
H	7.78	7.80	10.67
O	4.16	4.41	1.81
N	1.31	1.37	0.50
S	0.45	0.36	0.14
Ash	0.19	0.10	0.02
H_2 consumption, wt %	--	0.30	3.77
C_1-C_4 formation, wt %	--	0.40	0.80

a By osmometry

TABLE 2. LOW VOLTAGE MASS SPECTROMETRIC ANALYSIS OF UPGRADED
PRODUCT FOR POLYNUCLEAR AROMATIC COMPOUNDS
(13.8 MPa, 672 K, 0.5 LHSV)

Possible Structural Type (includes Alkyl derivatives)	Feedstock SRC I/II	Thermal-Treated over Alumina HR 8-1	Hydrotreated over Shell Ni-Mo HR 6-1
Benzenes	7.5	6.0	10.7
Naphthalenes	24.6	35.5	7.3
Indenes	3.9	3.1	8.4
Tetralins	13.0	10.1	38.0
Acenaphthylenes	13.1	9.0	9.0
Fluorenes	4.2	4.0	3.1
Phenanthrenes	6.1	3.6	2.2
Pyrenes	3.0	1.8	1.9
Chrysenes	0.4	0.4	1.7
Phenols	21.3	23.4	1.8

TABLE 3. DISTRIBUTION OF OXYGEN AND HYDROGEN IN THERMAL-
TREATED AND HYDROTREATED PRODUCTS

	Feedstock	Thermal-Treated HR 8-1	Hydrotreated HR 6-1
Total wt % O	4.16	4.41	1.81
IR Analysis			
wt % O as phenol	2.3	2.4	--
wt % as carbazole (NH)	0.3	0.3	Trace
PMR Analysis			
H_{aro}	0.371	0.375	0.118
H_α	0.302	0.302	0.217
H_{other}	0.327	0.323	0.665

TABLE 4. S, N DISTRIBUTION IN UPGRADED PRODUCT
Run HR 6-1 (Shell 324)

	Whole Product	IBP - 477 K	477-616 K	616 K+
Weight Percent of Product	100	27.6	42.7	29.6
Sp. Gravity, 289/289 K	0.938	0.830	0.933	1.102
Asphaltene, wt %	5.1	--	--	22.7
Benzene Insol, wt %	0.3	--	--	1.9
Viscosity, cps at 311 K	6.5	1.5	3.5	--
N, wt %	0.50	0.03	0.05	0.77
S, wt %	0.14	0.021	0.016	0.064
H/C	1.46	1.78	1.45	1.10
Hydrocarbon Type, vol %				
Aromatics	--	26	78	--
Olefins	--	< 1	< 1	--
Heterocyclics	--	5	< 1	--
Saturates	--	68	21	--

134

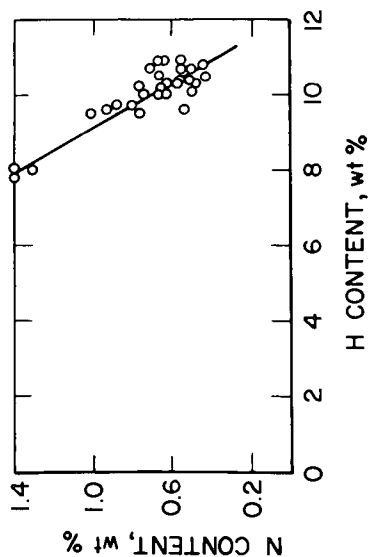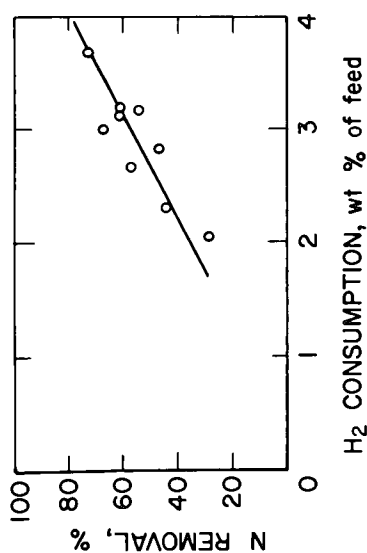Figure 2. Hydrogen-Carbon distribution in hydrocarbon components (Cx Hy).

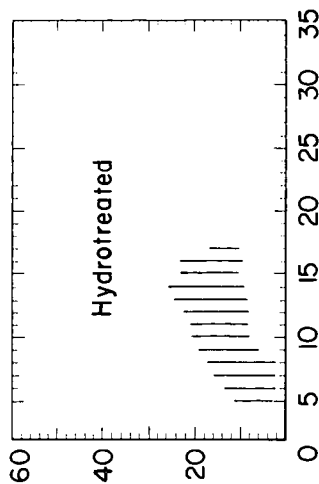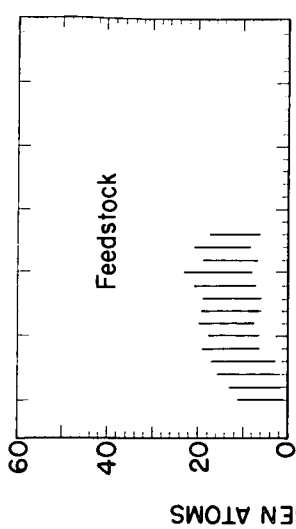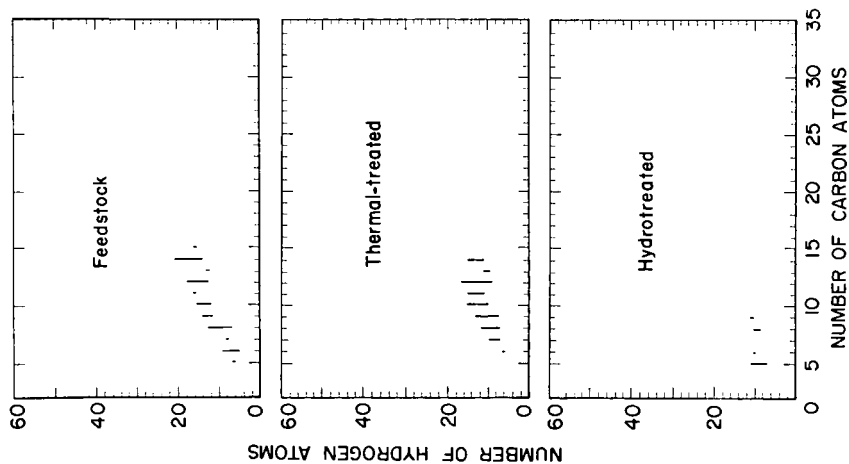Figure I. N Removal by hydrotreating in flow reactor.

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Figure 3. Hydrogen-Carbon distribution in heteroatom components (C_xH_yN)

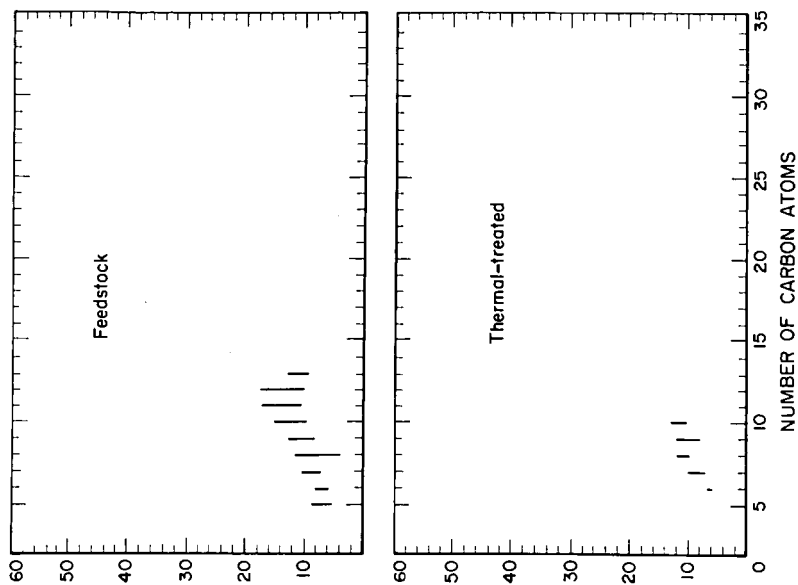Figure 4. Hydrogen-Carbon distribution in heteroatom components (C_xH_yO).
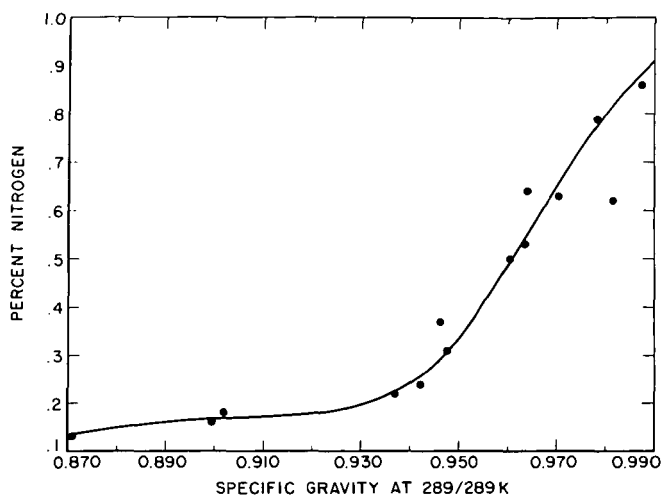
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136

Figure 5. Nitrogen content versus specific gravity for SRC product oil upgraded in continuous hydrotreater.
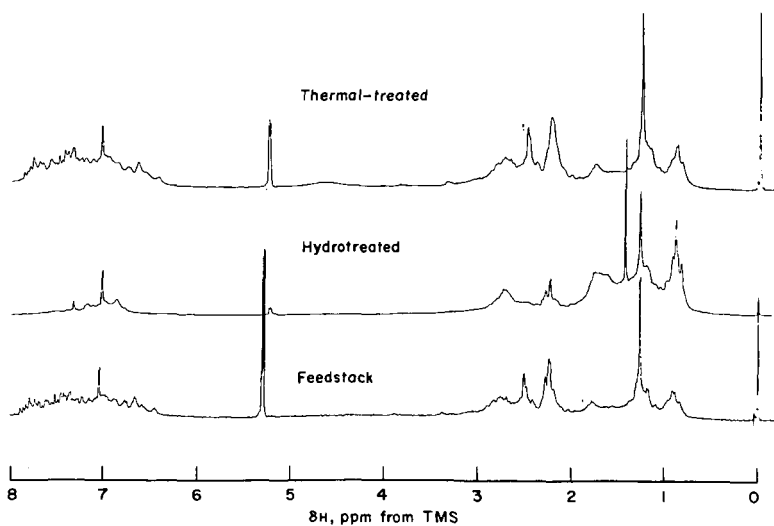

Figure 6. 100 MHz proton magnetic resonance spectra of SRC I/II blend and upgraded products.
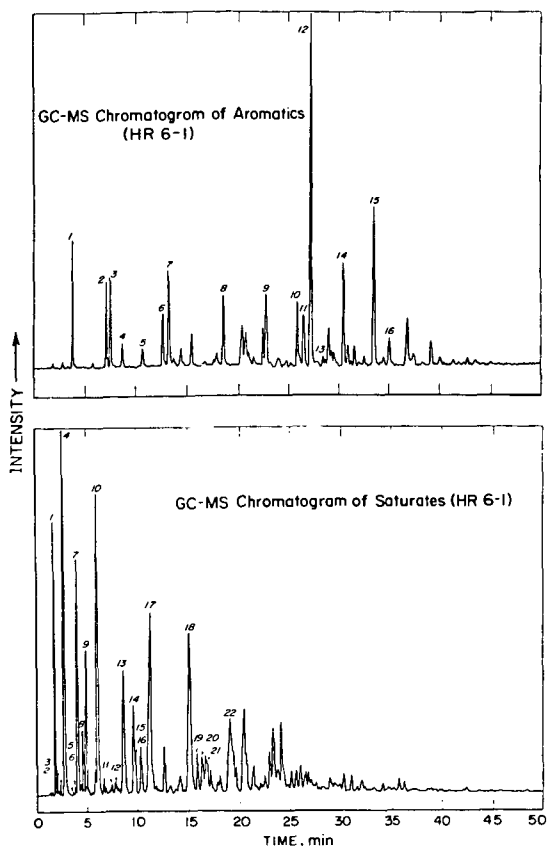
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137

Figure 7. GC-MS analysis of light fraction (IBP-477°K)
of hydrotreated coal liquid.

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	SATURATES	AROMATICS
Peak No.	Compounds	Compounds
1	Cyclohexane	Toluene
2	3-Methylhexane	Ethylbenzene
3	n-Heptane	m- and p-Xylene
4	Methylcyclohexane	o-Xylene
5	2-Methylheptane	C_3 - Benzene
6	3-Methylheptane	C_3 - Benzene
7	C_2 - Cyclohexane	C_3 - Benzene
8	C_2 - Cyclohexane	Indan
9	n-Octane and C_2 - Cyclohexane	Methylindan
10	C_2 - Cyclohexane	Methylindan
11	2-Methyloctane	Methylindan
12	3-Methyloctane	Tetralin
13	C_3 - Cyclohexane	Naphthalene
14	n-Nonane and C_3 - Cyclohexane	Methyltetralin
15	C_3 - Cyclohexane	Methyltetralin
16	C_3 - Cyclohexane	C_2 - Tetralin
17	C_3 - Cyclohexane	
18	C_4 - Cyclohexane	
19	C_4 - Cyclohexane	
20	C_4 - Cyclohexane	
21	n-Decane	
22	C_4 - Cyclohexane	

138